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PAPER

Ising exchange interaction in lanthanides and actinides

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Abstract

The Ising exchange interaction is a limiting case of strong exchange anisotropy and represents a key property of many magnetic materials. Here we find the necessary and sufficient conditions to achieve Ising exchange interaction for metal sites with unquenched orbital moments. Contrary to current views, the rules established here narrow much the range of lanthanide and actinide ions that can exhibit Ising exchange interaction. It is shown that the Ising interaction can be of two types: (i) coaxial, with magnetic moments directed along the anisotropy axes on the metal sites and (ii) non-coaxial, with arbitrary orientation of one of the magnetic moments. These findings will contribute to purposeful design of lanthanide- and actinide-based materials.

1. Introduction

Strong magnetic anisotropy on metal sites gives rise to novel magnetic properties, such as single-molecule magnet behavior [1, 2], magnetic multipole ordering [3, 4], and various exotic electronic phases [5, 6]. In lanthanides and actinides the spin–orbit coupling exceeds the crystal-field splitting of the ground ionic *LS* term leading to unquenched orbital momentum **L** [7]. As a result the low-lying spectrum on these metal ions is well described as crystal-field split eigenstates of the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where **S** is the spin of the corresponding term. If the symmetry of the metallic sites is lower than cubic, the ground crystal-field multiplet is either a Kramers doublet or a quasi doublet, for odd and even numbers of electrons on the metal ion, respectively. The presence of unquenched orbital momentum in these doublets makes them strongly anisotropic, which is also reflected in the strong anisotropy of their exchange interaction. The limit of this anisotropy is the exchange interaction of Ising type, which in the case of two interacting doublets or interacting doublet and isotropic spin has the form:

$$\hat{\mathrm{H}}_{\mathrm{I}} = \mathcal{J}\tilde{s}_{1z_1}\tilde{s}_{2z_2},$$
$$\hat{\mathrm{H}}_{\mathrm{I}} = \mathcal{J}\tilde{s}_{1z_1}\mathrm{S}_{2z_1}, \qquad (1)$$

where $\tilde{s}_i$ is the pseudospin 1/2 describing the doublet state of site *i*, S_2 is the isotropic spin of site 2, and z_i denotes the projection of pseudospin or isotropic spin along the main magnetic axis of doublet on site *i*.

Common beliefs concerning the Ising exchange coupling in lanthanides and actinides can be summarized with the following rules:

(1) The interaction involving quasi doublets of metal ions with an even number of electrons (the so-called Ising ions [3]) will always be the Ising type. However, in the case of metal ions with an odd number of electrons the Ising interaction is only achieved when the corresponding Kramers doublets have a zero magnetic moment in the transversal directions with respect to the main magnetic axis (i.e., are perfectly axial [8]) [3].

(2) In both of the above cases the Ising interaction is the *coaxial* type (1), when the local magnetic moments in the exchange states are directed either along the main magnetic axes z_i of the corresponding metal sites or, in the case of isotropic spin, along the main magnetic axis of the neighbor site (figure 1(a)) [9].

Rule (1) appears to be weakly restrictive predicting, in particular, Ising exchange interaction to all metal ions with even number of electrons. As discussed below, both these rules are based on an oversimplified treatment of

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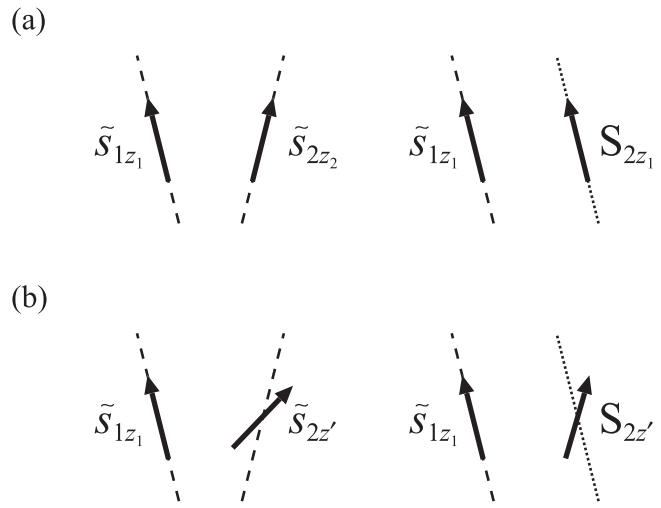

Figure 1. Two types of arrangement of local magnetic moments by the Ising exchange interaction: type I—coaxial (a) and type II—non-coaxial (b). The main magnetic axes on metal sites (dashed lines) are generally non-coplanar. The dotted lines indicate the main magnetic axis of the neighbor site.

the exchange interaction for metal ions with unquenched orbital momentum. Given the increasing interest in strongly anisotropic magnetic materials, the knowledge of precise conditions for the realization of the Ising exchange interaction between strongly anisotropic metal ions would be highly desirable.

In this work, the general conditions for achieving the Ising exchange interaction for metal sites with unquenched orbital momentum are found via analysis of the microscopic exchange Hamiltonian. These conditions are specified for interacting anisotropic metal ions in their doublet states and for such ions interacting with isotropic spins. Despite the overwhelming complexity of exchange interaction between centers with unquenched orbital moments, the realization of Ising exchange interaction has been shown to depend in most cases solely on the structure of doublet wave functions on the metal sites and not on the details of intersite interaction. This reduces the task of designing magnetic materials with Ising exchange interaction to create an appropriate crystal field on the metal sites.

2. Exchange interaction for *J*-multiplets

The ground-state (quasi) doublet wave functions in lanthanides and actinides can be written as a linear combination of eigenstates of the corresponding atomic *J*-multiplet:

$$|M\rangle = \sum_{m=-J}^{J} C_m |Jm\rangle,$$
$$|-M\rangle = \theta\, |M\rangle, \tag{2}$$

where θ is the operator of time inversion [10]. The composition of these wave functions is sensitive to the details of the local crystal field and can involve, in particular, all eigenfunctions $|Jm\rangle$. This means an adequate description of exchange interaction for these doublet states should involve an interacting Hamiltonian acting on the entire ground *J*-multiplet, i.e., expressed in terms of total angular momentum operator, J_α, $\alpha = x, y, z$. The latter was widely supposed to be of the Heisenberg-like form [3]:

$$\hat{H}_{\text{Heis}} = \mathcal{J}\mathbf{J}_1 \cdot \mathbf{J}_2. \tag{3}$$

Despite the lack of justification, this form is often used for the description of the interaction between lanthanides or actinides (or a similar form, $\propto \mathbf{J}_1 \cdot \mathbf{S}_2$, in the case of their interaction with an isotropic spin) [11–18]. Direct calculations show that with this form of exchange interaction the rules (1)–(2) hold true[1]. This is easily seen when we choose a particular form of wave functions (2) for strongly axial doublets:

$$\left|\pm M_i\right\rangle = \left|J_i \pm m_i\right\rangle, \quad i = 1, 2, \tag{4}$$

[1] The same is true for the phenomenological Lines model [19], $\hat{H}_{\text{Lines}} = \mathcal{J}\mathbf{S}_1 \cdot \mathbf{S}_2$, where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spins of the ground-state terms on the corresponding sites.

achievable either at high axial symmetry [8] or at strong axial component of the crystal field on sites [20]. Indeed, it can be checked directly that for odd numbers of electrons the transverse components of any angular momentum is zero for $m_i > 1/2$, while in the case of even number of electrons the smallest m_i for a quasi doublet (4) is $m_i = 1$ (the same is true for equation (2)) . Under such circumstances rules 1–2) and the conditions for zero transverse magnetization on metal ions (perfect axiality) hold true simultaneously[2].

We should note that the magnetic dipolar interaction between magnetic sites is also bilinear in total angular momentum operators albeit in a form different from equation (3):

$$\hat{\mathrm{H}}_{\mathrm{dip}} = -\frac{g_{\mathrm{L}}^2\mu_{\mathrm{B}}^2}{R_{12}^3}\Big[\mathbf{J}_1\cdot\mathbf{J}_2 - 3\big(\mathbf{J}_1\cdot\mathbf{n}_{12}\big)\big(\mathbf{J}_2\cdot\mathbf{n}_{12}\big)\Big], \tag{5}$$

where g_{L} is the Landé g factor, μ_{B} is the Bohr magneton, R_{12} is the distance between magnetic sites, and $\mathbf{n}_{12}$ is the normalized direction vector from site 1 to site 2. Therefore, it will also reduce to equation (1) when downfolded on the axial doublets (4) ($m_i > 1/2$). The corresponding constant $\mathcal{J}_{\mathrm{dip}}$ in (1) is a simple expression of the relative orientations of the local main magnetic axes and the vector connecting magnetic sites [9]. This interaction is considered dominant for pairs of lanthanides ions, which justifies the description of their interactions via bilinear operators (3) [11–18], as well as the validity of rules 1–2). Such a view is, however, ungrounded for simple reasons that (i) dipolar magnetic coupling can be diminished arbitrarily on geometric grounds and (ii) the exchange interaction can significantly exceed the dipolar coupling, especially when it is mediated by strongly covalent bridging groups [22]. In the cases of lanthanides interacting with isotropic spins (transition metals or radicals) and of interacting actinides (between themselves or with isotropic spins), the magnetic dipolar interaction is significantly smaller than the exchange interaction. The latter, however, is not described by the simple form (3) but represents a much more involved expression. In the case of two interacting ions with unquenched orbital momenta it has the form [4, 23]:

$$\hat{\mathrm{H}} = \sum_{kqk'q'}\mathcal{J}_{kqk'q'}\frac{O_k^q\big(\mathbf{J}_1\big)O_{k'}^{q'}\big(\mathbf{J}_2\big)}{O_k^0\big(J_1\big)O_{k'}^0\big(J_2\big)}, \tag{6}$$

where $\mathcal{J}_{kqk'q'}$ is the exchange parameter and $O_k^q(\mathbf{J}_1)$ and $O_{k'}^{q'}(\mathbf{J}_2)$ are Stevens operators[3] whose ranks k and k' have to obey the relation $k + k' =$ even due to the invariance of the Hamiltonian with respect to time inversion [10]. In equation (6), the terms such that one of k and k' is zero are not included because they are not exchange but crystal field. A metal ion with unquenched orbital momentum interacts with an isotropic spin as follows [23]:

$$\hat{\mathrm{H}} = \sum_{kqq'}\mathcal{J}_{kq1q'}\frac{O_k^q\big(\mathbf{J}_1\big)\mathrm{S}_{2q'}}{O_k^0\big(J_1\big)S_2}, \tag{7}$$

where k is odd due to the time reversal symmetry.

The highest rank k of Stevens operators entering equations (6) and (7) is found from the relation [23]:

$$k_{\max} = \min\Big[2l_1 + 1,\ 2J_1\Big], \tag{8}$$

where l_1 is the atomic orbital momentum and J_1 is the total angular momentum of the ground atomic multiplet on site 1 (a similar relation holds for $k'_{\max}$ on site 2). In the case of f^N ions, $k_{\max} = 2l + 1 = 7$ for $N = 2$–4 and 7–13, $k_{\max} = 2J = 5$ for $N = 1$,5, and $k_{\max} = 0$ for $N = 6$.

The maximal component q (>0) in equations (6) and (7) is generally determined by the details of intersite interaction [23]:

$$q_{\max} = \min\Big[\Delta^1_{\max} + 1,\ k_{\max}\Big], \tag{9}$$

where $\Delta^1_{\max}$ is the maximal difference of orbital momentum projections on site 1, m and n, entering as indices in the parameters $V_{mm'n'n}$ and $t^{12}_{mm'}t^{21}_{n'n}$, defining the direct and kinetic intersite exchange interaction, respectively (V is the bielectronic integral and t^{12}, t^{21} are electron transfer parameters). For low-symmetric systems, all these parameters will be non-zero, leading to $\Delta^1_{\max} = 2l_1$. Therefore, in such cases $q_{\max}$ is determined by intrasite properties only (as $k_{\max}$). The maximal value of q' at the second site, $q'_{\max}$, is determined in a similar way.

With the above information on the exchange interaction for the entire J multiplet, the effective Hamiltonian is derived. For more information on the exchange interaction, such as the form of $\mathcal{J}_{kqk'q'}$ and explanations of $k_{\max}$ and $q_{\max}$, see [23].

[2] A simplified treatment of kinetic exchange interaction within the so-called $1/U$ approximation [21] gives two interacting doublets (4) on Dy^{3+} ions an Ising exchange interaction similar to the first equation of (1). At the same time the interaction of one such Dy^{3+} doublet with an isotropic spin results in an Ising exchange, as in the second equation of (1), only for $m_1 = J_1 = 15/2$ (unpublished results).

[3] The Stevens operator is defined so that it transforms as spherical harmonics under rotation, which enables us to apply the Wigner–Eckart theorem (see, e.g., [24]).

3. Derivation of the effective exchange Hamiltonian

In this section, we derive the effective exchange Hamiltonian $\hat{\mathrm{H}}_{\mathrm{eff}}$ between the ground doublets of metal sites and between the ground doublet of the metal site and isotropic spin. This is done by projecting the complete form of the exchange Hamiltonian for the entire J-multiplet, equations (6) and (7), into the one within the truncated Hilbert space, and then describe the doublets by the $\tilde{s} = 1/2$ pseudospin operators. We consider first doublets of type (4), for which the derivation is the simplest.

3.1. Interacting axial doublets

Within the truncated Hilbert space, $\{|J_1\mu_1 J_2\mu_2\rangle\colon \mu_i = \pm m_i\}$, the exchange Hamiltonian (6) reduces to

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \hat{\mathrm{P}}_{12}\hat{\mathrm{H}}\hat{\mathrm{P}}_{12}, \tag{10}$$

where $\hat{\mathrm{P}}_{12} = \hat{\mathrm{P}}_1\hat{\mathrm{P}}_2$, and $\hat{\mathrm{P}}_i = \sum_{\mu_i}|J_i\mu_i\rangle\langle J_i\mu_i|$ $(i = 1, 2)$ is the projector into the truncated space. The matrix element of the exchange Hamiltonian (6) is

$$\left\langle J_1\mu_1' J_2\mu_2' \left|\hat{\mathrm{H}}\right| J_1\mu_1 J_2\mu_2\right\rangle = \sum_{kk'}\sum_{qq'}\mathcal{J}_{kqk'q'}\frac{C^{J_1\mu_1'}_{J_1\mu_1 kq}C^{J_2\mu_2'}_{J_2\mu_2 k'q'}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}, \tag{11}$$

using the Wigner–Eckart theorem and $C^{c\gamma}_{a\alpha b\beta}$ is the Clebsch–Gordan coefficients [25] [4]. Thus, substituting equation (11) into equation (10), the effective Hamiltonian is obtained as

$$\begin{aligned}
\hat{\mathrm{H}}_{\mathrm{eff}} = &\sum_{kk'}^{\mathrm{even}}\sum_{qq'}\frac{\mathcal{J}_{kqk'q'}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\
&\times\left[C^{J_1m_1}_{J_1m_1k0}\delta_{q,0}\left(\left|J_1m_1\right\rangle\left\langle J_1m_1\right| + \left|J_1 - m_1\right\rangle\left\langle J_1 - m_1\right|\right)\right.\\
&\left. + C^{J_1m_1}_{J_1-m_1k2m_1}\left(\delta_{q,2m_1}\left|J_1m_1\right\rangle\left\langle J_1 - m_1\right| + \delta_{q,-2m_1}\left|J_1 - m_1\right\rangle\left\langle J_1m_1\right|\right)\right]\\
&\times\left[C^{J_2m_2}_{J_2m_2k'0}\delta_{q',0}\left(\left|J_2m_2\right\rangle\left\langle J_2m_2\right| + \left|J_2 - m_2\right\rangle\left\langle J_2 - m_2\right|\right)\right.\\
&\left. + C^{J_2m_2}_{J_2-m_2k'2m_2}\left(\delta_{q',2m_2}\left|J_2m_2\right\rangle\left\langle J_2 - m_2\right| + \delta_{q',-2m_2}\left|J_2 - m_2\right\rangle\left\langle J_2m_2\right|\right)\right]\\
&+ \sum_{kk'}^{\mathrm{odd}}\sum_{qq'}\frac{\mathcal{J}_{kqk'q'}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\
&\times\left[C^{J_1m_1}_{J_1m_1k0}\delta_{q,0}\left(\left|J_1m_1\right\rangle\left\langle J_1m_1\right| - \left|J_1 - m_1\right\rangle\left\langle J_1 - m_1\right|\right)\right.\\
&\left. + C^{J_1m_1}_{J_1-m_1k2m_1}\left(\delta_{q,2m_1}\left|J_1m_1\right\rangle\left\langle J_1 - m_1\right| - \delta_{q,-2m_1}\left|J_1 - m_1\right\rangle\left\langle J_1m_1\right|\right)\right]\\
&\times\left[C^{J_2m_2}_{J_2m_2k'0}\delta_{q',0}\left(\left|J_2m_2\right\rangle\left\langle J_2m_2\right| - \left|J_2 - m_2\right\rangle\left\langle J_2 - m_2\right|\right)\right.\\
&\left. + C^{J_2m_2}_{J_2-m_2k'2m_2}\left(\delta_{q',2m_2}\left|J_2m_2\right\rangle\left\langle J_2 - m_2\right| - \delta_{q',-2m_2}\left|J_2 - m_2\right\rangle\left\langle J_2m_2\right|\right)\right].
\end{aligned} \tag{12}$$

Here, the property of the Clebsch–Gordan coefficient related to the time inversion is used [25]:

$$C^{c\gamma}_{a\alpha b\beta} = (-1)^{a+b-c}C^{c-\gamma}_{a-\alpha b-\beta}. \tag{13}$$

The two doublet functions (4) on site i can be put in correspondence to the eigenfunctions $|1/2, \pm 1/2\rangle$ of the pseudospin $\tilde{s}_i = 1/2$:

$$\left|J_im_i\right\rangle\left\langle J_im_i\right| = \frac{1}{2}\tilde{I}_i + \tilde{s}_{i0} = \frac{1}{2}\tilde{I}_i + \tilde{s}_{iz_i}, \tag{14}$$

$$\left|J_i - m_i\right\rangle\left\langle J_i - m_i\right| = \frac{1}{2}\tilde{I}_i - \tilde{s}_{i0}, = \frac{1}{2}\tilde{I}_i - \tilde{s}_{iz_i}, \tag{15}$$

$$\left|J_im_i\right\rangle\left\langle J_i - m_i\right| = -\sqrt{2}\,\tilde{s}_{i+1} = \tilde{s}_{i+} = \tilde{s}_{ix_i} + i\tilde{s}_{iy_i}, \tag{16}$$

$$\left|J_i - m_i\right\rangle\left\langle J_im_i\right| = \sqrt{2}\,\tilde{s}_{i-1} = \tilde{s}_{i-} = \tilde{s}_{ix_i} - i\tilde{s}_{iy_i}, \tag{17}$$

[4] We follow the convention of the spherical harmonics and the Clebsch–Gordan coefficients of [25].

where $i=1,2$, $\tilde{I}_i$ is the two-dimensional unit matrix, $\tilde{s}_{1\pm}=\tilde{s}_{1x_1}\pm i\tilde{s}_{1y_1}$ and $\tilde{s}_{2\pm}=\tilde{s}_{2x_2}\pm i\tilde{s}_{2y_2}$, and x_i and y_i denote the Cartesian axes of site i, which generally do not coincide with similar axes of another site. Using the 1/2-pseudospin operators,

$$\begin{aligned}\hat{\mathrm{H}}_{\mathrm{eff}}=&\sum_{kk'}^{\mathrm{even}}\sum_{qq'}\frac{\mathcal{J}_{kqk'q'}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\&\times\left[C^{J_1m_1}_{J_1m_1k0}\delta_{q,0}\tilde{I}_1+C^{J_1m_1}_{J_1-m_1k2m_1}\left(\delta_{q,2m_1}\tilde{s}_{1+}+\delta_{q,-2m_1}\tilde{s}_{1-}\right)\right]\\&\times\left[C^{J_2m_2}_{J_2m_2k'0}\delta_{q',0}\tilde{I}_2+C^{J_2m_2}_{J_2-m_2k'2m_2}\left(\delta_{q',2m_2}\tilde{s}_{2+}+\delta_{q',-2m_2}\tilde{s}_{2-}\right)\right]\\&+\sum_{kk'}^{\mathrm{odd}}\sum_{qq'}\frac{\mathcal{J}_{kqk'q'}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\&\times\left[C^{J_1m_1}_{J_1m_1k0}\delta_{q,0}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}+C^{J_1m_1}_{J_1-m_1k2m_1}\left(\delta_{q,2m_1}\tilde{s}_{1+}-\delta_{q,-2m_1}\tilde{s}_{1-}\right)\right]\\&\times\left[C^{J_2m_2}_{J_2m_2k'0}\delta_{q',0}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2}+C^{J_2m_2}_{J_2-m_2k'2m_2}\left(\delta_{q',2m_2}\tilde{s}_{2+}-\delta_{q',-2m_2}\tilde{s}_{2-}\right)\right].\end{aligned}\tag{18}$$

Finally, the general exchange interaction (6) projected onto doublet functions of the two sites can be recast in the following pseudospin-exchange Hamiltonian:

$$\begin{aligned}\hat{\mathrm{H}}_{\mathrm{eff}}=&\mathcal{J}_{II}\tilde{I}_1\tilde{I}_2+4\mathcal{K}_{zz}\tilde{s}_{1z_1}\tilde{s}_{2z_2}\\&+\mathcal{J}_{I+}\tilde{I}_1\tilde{s}_{2+}+\mathcal{J}_{I-}\tilde{I}_1\tilde{s}_{2-}+\mathcal{J}_{+I}\tilde{s}_{1+}\tilde{I}_2+\mathcal{J}_{-I}\tilde{s}_{1-}\tilde{I}_2\\&+2\mathcal{K}_{z+}\tilde{s}_{1z_1}\tilde{s}_{2+}+2\mathcal{K}_{z-}\tilde{s}_{1z_1}\tilde{s}_{2-}+2\mathcal{K}_{+z}\tilde{s}_{1+}\tilde{s}_{2z_2}+2\mathcal{K}_{-z}\tilde{s}_{1-}\tilde{s}_{2z_2}\\&+\left(\mathcal{J}_{++}+\mathcal{K}_{++}\right)\tilde{s}_{1+}\tilde{s}_{2+}+\left(\mathcal{J}_{+-}+\mathcal{K}_{+-}\right)\tilde{s}_{1+}\tilde{s}_{2-}\\&+\left(\mathcal{J}_{-+}+\mathcal{K}_{-+}\right)\tilde{s}_{1-}\tilde{s}_{2+}+\left(\mathcal{J}_{--}+\mathcal{K}_{--}\right)\tilde{s}_{1-}\tilde{s}_{2-}.\end{aligned}\tag{19}$$

Here, the parameters $\mathcal{J}$ and $\mathcal{K}$ are combinations of exchange parameters $\mathcal{J}_{kqk'q'}$ from equation (6) and products of the Clebsch–Gordan coefficients:

$$\mathcal{J}_{II}=\sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k0k'0}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2m_2k'0}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{20}$$

$$\mathcal{J}_{I\pm}=\mathcal{J}^{*}_{I\mp}=\frac{1+(-1)^{2m_2}}{2}\sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k0k'\pm2m_2}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{21}$$

$$\mathcal{J}_{\pm I}=\mathcal{J}^{*}_{\mp I}=\frac{1+(-1)^{2m_1}}{2}\sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k\pm2m_1k'0}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2m_2k'0}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{22}$$

$$\mathcal{J}_{\pm\pm}=\mathcal{J}^{*}_{\mp\mp}=\frac{1+(-1)^{2(m_1+m_2)}}{2}\sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k\pm2m_1k'\pm2m_2}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{23}$$

$$\mathcal{J}_{\pm\mp}=\mathcal{J}^{*}_{\mp\pm}=\frac{1+(-1)^{2(m_1+m_2)}}{2}\sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k\pm2m_1k'\mp2m_2}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{24}$$

$$\mathcal{K}_{zz}=\sum_{kk'}^{\mathrm{odd}}\mathcal{J}_{k0k'0}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2m_2k'0}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{25}$$

$$\mathcal{K}_{z\pm}=\mathcal{K}^{*}_{z\mp}=\pm\frac{1-(-1)^{2m_2}}{2}\sum_{kk'}^{\mathrm{odd}}\mathcal{J}_{k0k'\pm2m_2}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{26}$$

$$\mathcal{K}_{\pm z}=\mathcal{K}^{*}_{\mp z}=\pm\frac{1-(-1)^{2m_1}}{2}\sum_{kk'}^{\mathrm{odd}}\mathcal{J}_{k\pm2m_1k'0}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2m_2k'0}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{27}$$

$$\mathcal{K}_{\pm\pm}=\mathcal{K}^{*}_{\mp\mp}=\frac{1+(-1)^{2(m_1+m_2)}}{2}\sum_{kk'}^{\mathrm{odd}}\mathcal{J}_{k\pm2m_1k'\pm2m_2}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}},\tag{28}$$

$$\mathcal{K}_{\pm\mp}=\mathcal{K}^{*}_{\mp\pm}=-\frac{1+(-1)^{2(m_1+m_2)}}{2}\sum_{kk'}^{\mathrm{odd}}\mathcal{J}_{k\pm2m_1k'\mp2m_2}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}.\tag{29}$$

The above relations between exchange parameters are derived using the time reversal symmetry [10] and the symmetry relations for Clebsch–Gordan coefficients [25] (see appendix A.1).

The effective Hamiltonian (19) contains the constant part (the first term), the zero-field splitting (ZFS) part (terms 3–6), and the exchange part (the rest of the terms). With above equations we are able to identify the situations when $\mathcal{J}$ and $\mathcal{K}$ become zero[5]. The overview of such situations as a function of the parity of the number of electrons on sites (N_1 and N_2) and of the relation between $2m_i$ ($i = 1, 2$) and $q_{\max}$, $q'_{\max}$ (9) is given in appendix A.2. This information is sufficient to find the general conditions under which the exchange Hamiltonian for two interacting doublets (19) becomes the Ising type.

3.2. Interacting axial doublet and isotropic spin

In the case of a doublet (4) interacting with an isotropic spin, the derivations are similar. Now we only need to consider the matrix elements of operators referring to the first site in equation (7):

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \hat{\mathrm{P}}_1 \hat{\mathrm{H}} \hat{\mathrm{P}}_1. \tag{30}$$

The matrix elements of $\hat{\mathrm{H}}$ (7) are given as

$$\left\langle J_1 \mu'_1 \left| \hat{\mathrm{H}} \right| J_1 \mu_1 \right\rangle = \sum_{kqq'} \mathcal{J}_{kq1q'} \frac{C^{J_1 \mu'_1}_{J_1 \mu_1 kq} \mathrm{S}_{2q'}}{C^{J_1 J_1}_{J_1 J_1 k0} S_2}, \tag{31}$$

and the projected exchange Hamiltonian looks as follows:

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \sum_{q'=-1}^{1} \left[2\mathcal{K}_{zq'} \tilde{s}_{1z_1} + \mathcal{K}_{+q'} \tilde{s}_{1+} + \mathcal{K}_{-q'} \tilde{s}_{1-} \right] \frac{\mathrm{S}_{2q'}}{S_2}. \tag{32}$$

Here, the spherical components for $\mathbf{S}_2$ are used [25] and the expressions for parameters $\mathcal{K}$ are given as

$$\mathcal{K}_{zq'} = \sum_{k}^{\mathrm{odd}} \mathcal{J}_{k01q'} \frac{C^{J_1 m_1}_{J_1 m_1 k0}}{C^{J_1 J_1}_{J_1 J_1 k0}}, \tag{33}$$

$$\mathcal{K}_{\pm q'} = \pm \sum_{k}^{\mathrm{odd}} \mathcal{J}_{k\pm 2m_1 1q'} \frac{C^{J_1 m_1}_{J_1 -m_1 k 2m_1}}{C^{J_1 J_1}_{J_1 J_1 k0}}. \tag{34}$$

As in the previous case, equation (19), the exchange Hamiltonian (32) can become the Ising type under certain conditions.

4. Two types of Ising exchange interaction

With the use of the properties of $\mathcal{J}$ and $\mathcal{K}$ in section 3, we discuss the form of the effective pseudospin Hamiltonian. Based on the analysis, we show that there are two types of Ising Hamiltonian.

Consider, for example, a situation when both N_1 and N_2 are odd. For $m_1 > q_{\max}/2$ and $m_2 > q'_{\max}/2$, we obtain all parameters in equation (19) zero except $\mathcal{K}_{zz}$, resulting in

$$\hat{\mathrm{H}}_{\mathrm{I}} = 4\mathcal{K}_{zz} \tilde{s}_{1z_1} \tilde{s}_{2z_2}, \tag{35}$$

i.e., an Ising Hamiltonian of coaxial type (1), with an ordering of magnetic moments shown in the left plot of figure 1(a).

If we diminish the axiality of site 2 so that $m_1 > q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$, equation (19) reduces to

$$\hat{\mathrm{H}}_{\mathrm{eff}} = 4\mathcal{K}_{zz} \tilde{s}_{1z_1} \tilde{s}_{2z_2} + 2\mathcal{K}_{z+} \tilde{s}_{1z_1} \tilde{s}_{2+} + 2\mathcal{K}_{z-} \tilde{s}_{1z_1} \tilde{s}_{2-}, \tag{36}$$

where all terms contain $\tilde{s}_{1z_1}$. The expression multiplying the latter is a combination of pseudospin operators of the second site, which can be written in the form

$$\tilde{s}_{2z'} = \frac{\Re\left(\mathcal{K}_{z+}\right)}{\mathcal{K}'_{zz'}} \tilde{s}_{2x_2} - \frac{\Im\left(\mathcal{K}_{z+}\right)}{\mathcal{K}'_{zz'}} \tilde{s}_{2y_2} + \frac{\mathcal{K}_{zz}}{\mathcal{K}'_{zz'}} \tilde{s}_{2z_2},$$
$$\mathcal{K}'_{zz'} = \sqrt{\mathcal{K}_{zz}^2 + \left|\mathcal{K}_{z+}\right|^2}. \tag{37}$$

Since the coefficients in the first equation are real and normalized to unity, the corresponding combination of pseudospin projections can be viewed as a rotated pseudospin from initial direction z_2 toward a new direction z'. Accordingly, the coefficients are directional cosines of the z' axis in the coordinate system of site 2. Despite the fact that the pseudospin is not related to any physical angular momentum but only defined via Pauli matrices on

[5] The ZFS terms only appear when at least one metal ion is the non-Kramers type (integer J_1 and J_2) and look artifactual (are not invariant under time reversal) because we describe non-Kramers ions by pseudospins $\tilde{s} = 1/2$. This drawback disappears when the description of such ions is done with integer pseudospins, e.g., $\tilde{s} = 1$ [26]. This is not necessary here because the exchange part (which is only of interest here) is described correctly already within such a simplified treatment.

Table 1. Exchange interaction between two doublets and between a doublet and an isotropic spin. I and II denote the two types of Ising exchange interaction, equations (1), (35) and equations (38), (39), respectively; N stands for a non-Ising exchange interaction.

N_2 \ N_1		Odd		Even	
		$m_1 > q_{\max}/2$	$m_1 \leqslant q_{\max}/2$	$m_1 > q_{\max}/2$	$m_1 \leqslant q_{\max}/2$
Odd	$m_2 > q'_{\max}/2$	I	II	I	N
Odd	$m_2 \leqslant q'_{\max}/2$	II	N	II	N
Even	$m_2 > q'_{\max}/2$	I	II	I	N
Even	$m_2 \leqslant q'_{\max}/2$	N	N	N	N
isotropic spin		II	N	II	N

the basis of two states (4), we can still define its rotation via induced transformations of the doublet wave functions [27]. Then the eigenfunctions of the new pseudospin operator $\tilde{s}_{2z'}$ will be the same functions (4) defined with respect to rotated quantization axis z', i.e., $|J_i \pm m_i\rangle'$. Then equation (36) is rewritten as

$$\hat{\mathrm{H}}_{\mathrm{II}} = 4\mathcal{K}'_{zz'}\tilde{s}_{1z_1}\tilde{s}_{2z'}, \tag{38}$$

which has the form of an Ising Hamiltonian of *non-coaxial* type because the magnetization at the second site will not be directed along the corresponding main magnetic axis z_2 but along a different axis z' (left plot in figure 1(b)). This makes it qualitatively different from the coaxial Ising interaction described by equations (1) and (35). Accordingly, the two Ising interactions will be called hereafter type I and II.

On the other hand, the interaction of a doublet (4) with an isotropic spin, equation (32), can only become the Ising type if both parameters $\mathcal{K}_{+q'}$ and $\mathcal{K}_{-q'}$ are zero. This is achieved when $m_1 > q_{\max}/2$, in which case the Hamiltonian (32) becomes the form:

$$\hat{\mathrm{H}}_{\mathrm{II}} = 2\mathcal{K}'_{zz'}\tilde{s}_{1z_1}\frac{\mathrm{S}_{2z'}}{S_2},$$
$$\mathcal{K}'_{zz'} = \sqrt{\left|\mathcal{K}_{z0}\right|^2 + \left|\mathcal{K}_{z+1}\right|^2 + \left|\mathcal{K}_{z-1}\right|^2}, \tag{39}$$

in which the combination

$$\mathrm{S}_{2z'} = \sum_{q'=-1}^{1}\frac{\mathcal{K}_{zq'}\mathrm{S}_{2q'}}{\mathcal{K}'_{zz'}} \tag{40}$$

is a rotated spin S_{2z} from direction z_1 to z'. This means the Hamiltonian (39) is the non-coaxial Ising type, in which the magnetic moment on site 2 points to a direction different from the main magnetic axis on site 1, as indicated in the right plot of figure 1(b) (cf figure 1(a)). Note that the Ising interaction of type I is only achieved when $\mathcal{K}_{z\pm1}$ in equation (40) are both zero, which requires special symmetry of the exchange bridge.

The classification for all cases is shown in appendix B and table 1 summarizes our main results. It shows that rule 2) (Ising interaction type I) is not satisfied in most cases. We can also see that the type of resulting exchange Hamiltonian merely depends on the relative values of m_1, m_2, and $q_{\max}/2$, $q'_{\max}/2$, respectively. Then we can generalize the results in table 1 over arbitrary doublets (2) if by m_1 and m_2 we will understand not particular doublets (4) but the minimal absolute values of the index m in the expansion of the corresponding doublet wave function $|M\rangle$ in equation (2).

5. Ising metal ions

Table 1 shows that rule 1) does not hold either. Instead, the realization of the Ising exchange interaction depends on the value of $q_{\max}$ ($q'_{\max}$), which is determined by the smaller of the quantities $\Delta_{\max} + 1$ and $k_{\max}$ (equation (9)). $\Delta_{\max}$ is small only for sufficiently high symmetry of the exchange bridge. For instance, in the case of a linear bridge (figure 2(a)) it can have the smallest possible value, $\Delta_{\max} = 0$. Its value increases fast with lowering of the symmetry of the bridge, and the accompanying increase of the mixing of m orbitals, which is 2 for the case shown in figure 2(b) and 4 for the case shown in figure 2(c). When $\Delta^{1,2}_{\max}$ on sites become sufficiently large, $q_{\max}$ ($q'_{\max}$) is determined by $k_{\max}$ ($k'_{\max}$), equation (8), i.e., the smaller of the quantities $2l_i + 1$ (= 7 for f orbitals) and $2J_i$ on corresponding sites. Designing a strongly axial crystal field on sites we can achieve m_i values as high as J_i [9]. Then such ions with $J_i > 7/2$ will *a priori* provide Ising exchange interaction with any other magnetic site according to table 1. Contrary to what is stated by rule 1), these are precisely the ones that can be called Ising ions. They are listed in table 2.

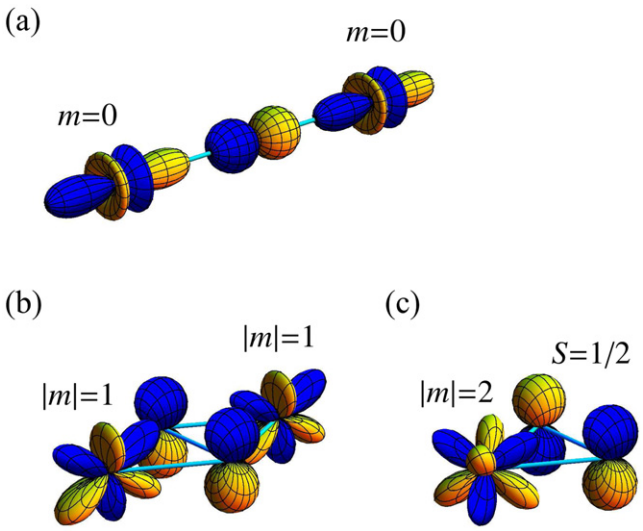

Figure 2. Examples of symmetric superexchange interaction: (a) via p_σ orbital of a single bridging atom, connecting only $m=0$ orbitals on lanthanide sites; (b) via the highest occupied orbital of the N_2^{2-} bridge [28], promoting interaction between $m=\pm1$ orbitals on lanthanide sites; and (c) unpaired electron ($S=1/2$) at N_2^{3-} [28] interacting only with $m=\pm2$ orbitals of lanthanide due to symmetry restrictions.

Table 2. Ising metal ions. Only valencies of metal ions in known complexes are listed [7, 29].

M^{n+} \ f^N	f^2	f^3	f^4	f^8	f^9	f^{10}	f^{11}	f^{12}
Ln^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}
Ac^{2+}							Es^{2+}	
Ac^{3+}		U^{3+}	Np^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}		
Ac^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Cf^{4+}				
Ac^{5+}	Np^{5+}	Pu^{5+}						
Ac^{6+}	Pu^{6+}							

6. Conclusions

In this work, we find necessary and sufficient conditions to achieve Ising exchange interaction in materials involving lanthanide and actinide metal ions. Unless the symmetry of the exchange bridge is not very high, these conditions are determined solely by the electronic properties of individual metal ions. According to these conditions, by far not all metal ions can display Ising exchange interaction (table 2). We also find that two types of Ising exchange interaction can arise in these systems: the coaxial and non-coaxial ones. In particular, it is established that the Ising interaction between an anisotropic doublet and an isotropic spin is the second type. The basic property of Ising coupling is the lack of dynamics in the resulting exchange doublets, which is also in the applied magnetic field. This condition is indispensable for achieving single-molecule magnets since it ensures the quenching of quantum tunneling of magnetization in individual exchange doublets. The insight gained in this work will contribute to purposeful design of lanthanide and actinide based materials.

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Note added in proof. The Ising exchange interaction between strongly axial ions (Dy, Ho) has been recently addressed in the preprint [30] with a different approach from the present work.

Appendix A. Exchange parameters for the effective model

The relations between exchange parameters, (20)–(29), are derived here. In the derivation, we use the property of the exchange parameter under time inversion [23]:

$$\mathcal{J}^{*}_{kqk'q'} = (-1)^{q+q'}\mathcal{J}_{k-qk'-q'}, \tag{A.1}$$

and the property of the Clebsch–Gordan coefficients [25]:

$$C^{c\gamma}_{a\alpha b\beta} = (-1)^{b+\beta}\sqrt{\frac{2c+1}{2a+1}}\,C^{a-\alpha}_{c-\gamma b\beta}. \tag{A.2}$$

A.1. Exchange parameters of $\hat{\mathrm{H}}_{\mathrm{eff}}$

The relations between the exchange parameters of $\hat{\mathrm{H}}_{\mathrm{eff}}$, $\mathcal{J}$ and $\mathcal{K}$ (20)–(29), are derived. We obtain the form of $\mathcal{J}$ and $\mathcal{K}$ expanding equation (18). Among the exchange parameters, $\mathcal{J}_{II}$ (20) and $\mathcal{K}_{zz}$ (25) are obtained by this direct calculation, whereas for the others, additional calculations with equations (A.1) and (A.2) are required.

- $\mathcal{J}_{I\pm}$ and $\mathcal{J}_{\pm I}$, equations (21), (22):
  Using equation (A.1),

$$\begin{aligned}\mathcal{J}_{I\pm} &= \sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k0k'\pm 2m_2}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\ &= (-1)^{\pm 2m_2}\sum_{kk'}^{\mathrm{even}}\left(\mathcal{J}_{k0k'\mp 2m_2}\right)^{*}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\ &= (-1)^{2m_2}\mathcal{J}^{*}_{I\mp}.\end{aligned} \tag{A.3}$$

  Since m_2 is an integer or half-integer, $(-1)^{2m_2} = (-1)^{-2m_2}$. On the other hand, applying equation (A.2) to site 2,

$$\begin{aligned}\mathcal{J}_{I\pm} &= \sum_{kk'}^{\mathrm{even}}(-1)^{k'+2m_2}\mathcal{J}_{k0k'\pm 2m_2}\frac{C^{J_1m_1}_{J_1m_1k0}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\ &= (-1)^{2m_2}\mathcal{J}_{I\pm}.\end{aligned} \tag{A.4}$$

  Since k' is even, $(-1)^{k'} = 1$. Therefore,

$$\mathcal{J}_{I\pm} = (-1)^{2m_2}\mathcal{J}_{I\pm} = \mathcal{J}^{*}_{I\mp}, \tag{A.5}$$

  and we obtain equation (21). Similarly, we obtain equation (22).

- $\mathcal{J}_{\pm\pm}$, equation (23):
  Using equation (A.1),

$$\begin{aligned}\mathcal{J}_{\pm\pm} &= \sum_{kk'}^{\mathrm{even}}\mathcal{J}_{k\pm 2m_1k'\pm 2m_2}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\ &= (-1)^{2(m_1+m_2)}\sum_{kk'}^{\mathrm{even}}\left(\mathcal{J}_{k\mp 2m_1k'\mp 2m_2}\right)^{*}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\ &= (-1)^{2(m_1+m_2)}\mathcal{J}^{*}_{\mp\mp}.\end{aligned} \tag{A.6}$$

  Using equation (A.2) for both sites,

$$\begin{aligned}\mathcal{J}_{\pm\pm} &= \sum_{kk'}^{\mathrm{even}}(-1)^{k+2m_1+k'+2m_2}\mathcal{J}_{k\pm 2m_1k'\pm 2m_2}\frac{C^{J_1m_1}_{J_1-m_1k2m_1}C^{J_2m_2}_{J_2-m_2k'2m_2}}{C^{J_1J_1}_{J_1J_1k0}C^{J_2J_2}_{J_2J_2k'0}}\\ &= (-1)^{2(m_1+m_2)}\mathcal{J}_{\pm\pm}.\end{aligned} \tag{A.7}$$

  From these equations,

$$\mathcal{J}_{\pm\pm} = (-1)^{2(m_1+m_2)}\mathcal{J}_{\pm\pm} = (-1)^{2(m_1+m_2)}\mathcal{J}^{*}_{\mp\mp}, \tag{A.8}$$

  and we obtain relation (23).

- $\mathcal{J}_{\pm\mp}$, equation (24):
  Using equation (A.1),

$$\mathcal{J}_{\pm\mp} = \sum_{kk'}^{\text{even}} \mathcal{J}_{k\pm 2m_1 k' \mp 2m_2} \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2(m_1+m_2)} \sum_{kk'}^{\text{even}} \left(\mathcal{J}_{k\mp 2m_1 k' \pm 2m_2} \right)^* \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2m_1+2m_2} \mathcal{J}^*_{\mp\pm}. \tag{A.9}$$

Using equation (A.2) for both sites,

$$\mathcal{J}_{\pm\mp} = \sum_{kk'}^{\text{even}} (-1)^{k+2m_1+k'+2m_2} \mathcal{J}_{k\pm 2m_1 k' \mp 2m_2} \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2(m_1+m_2)} \mathcal{J}_{\pm\mp}. \tag{A.10}$$

Combining these relations,

$$\mathcal{J}_{\pm\mp} = (-1)^{2(m_1+m_2)} \mathcal{J}_{\pm\mp} = (-1)^{2(m_1+m_2)} \mathcal{J}^*_{\mp\pm}, \tag{A.11}$$

and we obtain equation (24).

- $\mathcal{K}_{z\pm}$, $\mathcal{K}_{\pm z}$, equations (26), (27):
  Using equation (A.1),

$$\mathcal{K}_{z\pm} = \pm \sum_{kk'}^{\text{odd}} \mathcal{J}_{k0k' \pm 2m_2} \frac{C^{J_1 m_1}_{J_1 m_1 k 0} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= \pm (-1)^{2m_2} \sum_{kk'}^{\text{odd}} \left(\mathcal{J}_{k0k' \mp 2m_2} \right)^* \frac{C^{J_1 m_1}_{J_1 m_1 k 0} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= - (-1)^{2m_2} \mathcal{K}^*_{z\mp}. \tag{A.12}$$

  Using equation (A.2) for site 2,

$$\mathcal{K}_{z\pm} = \pm \sum_{kk'}^{\text{odd}} (-1)^{k'+2m_2} \mathcal{J}_{k0k' \pm 2m_2} \frac{C^{J_1 m_1}_{J_1 m_1 k 0} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= - (-1)^{2m_2} \mathcal{K}_{z\pm}. \tag{A.13}$$

  Here, we used that k' is odd. Therefore, we obtain

$$\mathcal{K}_{z\pm} = -(-1)^{2m_2} \mathcal{K}_{z\pm} = -(-1)^{2m_2} \mathcal{K}^*_{z\mp}, \tag{A.14}$$

  and equation (26). Similarly, we obtain equation (27).

- $\mathcal{K}_{\pm\pm}$, equation (28):
  Using equation (A.1),

$$\mathcal{K}_{\pm\pm} = \sum_{kk'}^{\text{odd}} \mathcal{J}_{k\pm 2m_1 k' \pm 2m_2} \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2(m_1+m_2)} \sum_{kk'}^{\text{odd}} \left(\mathcal{J}_{k\mp 2m_1 k' \mp 2m_2} \right)^* \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2(m_1+m_2)} \mathcal{K}^*_{\mp\mp}. \tag{A.15}$$

  Using equation (A.2) for both sites,

$$\mathcal{K}_{\pm\pm} = \sum_{kk'}^{\text{odd}} (-1)^{k+2m_1+k'+2m_2} \mathcal{J}_{k\pm 2m_1 k' \pm 2m_2} \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2(m_1+m_2)} \mathcal{K}_{\pm\pm}. \tag{A.16}$$

  Therefore,

$$\mathcal{K}_{\pm\pm} = (-1)^{2(m_1+m_2)} \mathcal{K}_{\pm\pm} = (-1)^{2(m_1+m_2)} \mathcal{K}^*_{\mp\mp}. \tag{A.17}$$

- $\mathcal{K}_{\pm\mp}$, equation (29):
  Using equation (A.1),

$$\mathcal{K}_{\pm\mp} = -\sum_{kk'}^{\text{odd}} \mathcal{J}_{k\pm 2m_1 k'\mp 2m_2} \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= -(-1)^{2(m_1+m_2)} \sum_{kk'}^{\text{odd}} \left(\mathcal{J}_{k\mp 2m_1 k'\pm 2m_2} \right)^* \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2m(m_1+m_2)} \mathcal{K}^*_{\mp\pm}. \tag{A.18}$$

Using equation (A.2) for both sites,

$$\mathcal{K}_{\pm\mp} = -\sum_{kk'}^{\text{odd}} (-1)^{k+2m_1+k'+2m_2} \mathcal{J}_{k\pm 2m_1 k'\mp 2m_2} \frac{C^{J_1 m_1}_{J_1 - m_1 k 2m_1} C^{J_2 m_2}_{J_2 - m_2 k' 2m_2}}{C^{J_1 J_1}_{J_1 J_1 k 0} C^{J_2 J_2}_{J_2 J_2 k' 0}}$$
$$= (-1)^{2m_1+2m_2} \mathcal{K}_{\pm\mp}. \tag{A.19}$$

Therefore,

$$\mathcal{K}_{\pm\mp} = (-1)^{2(m_1+m_2)} \mathcal{K}_{\pm\mp} = (-1)^{2(m_1+m_2)} \mathcal{K}^*_{\mp\pm}, \tag{A.20}$$

and we obtain equation (29).

A.2. Symmetry properties

Some of $\mathcal{J}$ and $\mathcal{K}$ become zero due to (i) time reversal symmetry and (ii) the structure of the exchange interaction.

(i) Time reversal symmetry:
When the magnetic site has an odd (even) number of electrons, the total angular momentum and its projection m_i are half-integers (integers), and thus, $(-1)^{2m_i} = -1\,(=1)$. Due to the change in sign, some of $\mathcal{J}$ and $\mathcal{K}$ (20)–(29) become zero. The results are summarized as follows:

- $\mathcal{J}_{I\pm} = 0$ when N_2 is odd,
- $\mathcal{J}_{\pm I} = 0$ when N_1 is odd,
- $\mathcal{K}_{z\pm} = 0$ when N_2 is even,
- $\mathcal{K}_{\pm z} = 0$ when N_1 is even,
- $\mathcal{J}_{\pm\pm} = \mathcal{J}_{\pm\mp} = 0$ when one of N_1 and N_2 is odd,
- $\mathcal{K}_{\pm\pm} = \mathcal{K}_{\pm\mp} = 0$ when one of N_1 and N_2 is even,

where N_1 and N_2 are the numbers of electrons on sites 1 and 2, respectively.

(ii) Structure of the exchange Hamiltonian:
The values of the exchange parameters $\mathcal{J}$ and $\mathcal{K}$ depend on $q_{\max}$ (9). For large $m_i > q_{\max}/2$, some of $\mathcal{J}$ and $\mathcal{K}$ are zero because either the Clebsch–Gordan coefficient C^{Jm}_{J-mk2m} or $\mathcal{J}_{kqk'q'}$ becomes zero. See the details below.

First, we consider a non-symmetric system where $q_{\max}$ corresponds to $k_{\max}$. In this case, $\mathcal{J}$ and $\mathcal{K}$ become zero only when $C^{Jm}_{J-mk2m} = 0$, which holds when $k > 2m$. Since the maximum of k is fixed, we have to further consider two cases regarding J:

(a) $J_i \leqslant l_i + 1/2$ and $k_{\max} = q_{\max} = 2J_i$:
Since $2m \leqslant k_{\max}$ is always satisfied, the Clebsch–Gordan coefficients are in general nonzero, $C^{Jm}_{J-mk_{\max}2m} \neq 0$. Therefore, all $\mathcal{J}$ and $\mathcal{K}$ can be nonzero due to the reason different from time reversal symmetry.

(b) $J_i > l_i + 1/2$ and $k_{\max} = q_{\max} = 2(l_i + 1/2)$:
It is possible to have m, which is larger than $k_{\max}/2$. In this case, we obtain $C^{Jm}_{J-mk_{\max}2m} = 0$, and $\mathcal{J}$ and $\mathcal{K}$ which include the Clebsch–Gordan coefficient become zero.

The case of $N = 6$ ($J = 0$) is not considered since the ion is nonmagnetic. The above discussion is summarized as follows:

- $\mathcal{J}_{\pm I} = \mathcal{J}_{\pm\pm} = \mathcal{J}_{\pm\mp} = \mathcal{K}_{\pm z} = \mathcal{K}_{\pm\pm} = \mathcal{K}_{\pm\mp} = 0$ when $m_1 > l_1 + 1/2$,

- $\mathcal{J}_{I\pm} = \mathcal{J}_{\pm\pm} = \mathcal{J}_{\pm\mp} = \mathcal{K}_{z\pm} = \mathcal{K}_{\pm\pm} = \mathcal{K}_{\pm\mp} = 0$ when $m_2 > l_2 + 1/2$.

In symmetric systems, $q_{\max} \leqslant k_{\max}$, and the condition changes. Contrary to the non-symmetric case, $\mathcal{J}$ and $\mathcal{K}$ become zero for m such that $k_{\max} > 2m > q_{\max} \geqslant 0$, because C^{Jm}_{J-mk2m} is not zero for $k \geqslant 2m$, while $\mathcal{J}_{k2mk'q'} = 0$. The selection rule becomes

- $\mathcal{J}_{\pm I} = \mathcal{J}_{\pm\pm} = \mathcal{J}_{\pm\mp} = \mathcal{K}_{\pm z} = \mathcal{K}_{\pm\pm} = \mathcal{K}_{\pm\mp} = 0$ when $m_1 > q_{\max}/2$,
- $\mathcal{J}_{I\pm} = \mathcal{J}_{\pm\pm} = \mathcal{J}_{\pm\mp} = \mathcal{K}_{z\pm} = \mathcal{K}_{\pm\pm} = \mathcal{K}_{\pm\mp} = 0$ when $m_2 > q'_{\max}/2$.

Appendix B. Classification of the effective Hamiltonians

With the use of the conditions given in appendix A.2, we study the structure of the effective Hamiltonian, (19) and (32), for all cases. The effective Hamiltonian is classified into three types: Ising I, Ising II, and non-Ising. Ising I does not change the magnetic axes due to the exchange interaction, while Ising II does.

B.1. Doublets with unquenched orbital momentum

The form of the effective Hamiltonian between anisotropic doublets (19) becomes as follows (the condition for the non-symmetric case is obtained by replacing $q_{\max}$ by $l + 1/2$):

(i) Both N_1 and N_2 are odd (m_1 and m_2 are half-integers).

(a) $m_1 > q_{\max}/2$ and $m_2 > q'_{\max}/2$ (Ising, I)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2}. \tag{B.1}$$

(b) $m_1 > q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$ (Ising, II)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + \mathcal{K}_{z+}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2+} + \mathcal{K}_{z-}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2-} \tag{B.2}$$

$$= \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}'_{zz'}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z'}}{\tilde{s}_2}, \tag{B.3}$$

where

$$\mathcal{K}'_{zz'} = \sqrt{\mathcal{K}^2_{zz} + \left|\mathcal{K}_{z+}\right|^2}, \tag{B.4}$$

$$\tilde{s}_{2z'} = \frac{\Re\left(\mathcal{K}_{z+}\right)}{\mathcal{K}'_{zz'}}\tilde{s}_{2x_2} - \frac{\Im\left(\mathcal{K}_{z+}\right)}{\mathcal{K}'_{zz'}}\tilde{s}_{2y_2} + \frac{\mathcal{K}_{zz}}{\mathcal{K}'_{zz'}}\tilde{s}_{2z_2}. \tag{B.5}$$

(c) $m_1 \leqslant q_{\max}/2$ and $m_2 > q'_{\max}/2$ (Ising, II)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + \mathcal{K}_{+z}\tilde{s}_{1+}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + \mathcal{K}_{-z}\tilde{s}_{1-}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} \tag{B.6}$$

$$= \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}'_{z'z}\frac{\tilde{s}_{1z'}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2}, \tag{B.7}$$

where

$$\mathcal{K}'_{zz} = \sqrt{\mathcal{K}^2_{zz} + \left|\mathcal{K}_{+z}\right|^2}, \tag{B.8}$$

$$\tilde{s}_{1z'} = \frac{\Re\left(\mathcal{K}_{+z}\right)}{\mathcal{K}'_{z'z}}\tilde{s}_{1x_1} - \frac{\Im\left(\mathcal{K}_{+z}\right)}{\mathcal{K}'_{z'z}}\tilde{s}_{1y_1} + \frac{\mathcal{K}_{zz}}{\mathcal{K}'_{z'z}}\tilde{s}_{1z_1}. \tag{B.9}$$

(d) $m_1 \leqslant q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$ (non-Ising)

$$\begin{aligned}\hat{\mathrm{H}}_{\mathrm{eff}} = {} & \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} \\ & + \mathcal{K}_{z+}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2+} + \mathcal{K}_{z-}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2-} \\ & + \mathcal{K}_{+z}\tilde{s}_{1+}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + \mathcal{K}_{-z}\tilde{s}_{1-}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} \\ & + \mathcal{K}_{++}\tilde{s}_{1+}\tilde{s}_{2+} + \mathcal{K}_{+-}\tilde{s}_{1+}\tilde{s}_{2-} \\ & + K_{-+}\tilde{s}_{1-}\tilde{s}_{2+} + K_{--}\tilde{s}_{1-}\tilde{s}_{2-}\end{aligned} \tag{B.10}$$

$$\begin{aligned} = {} & J_{II}\tilde{I}_1\tilde{I}_2 + K_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} \\ & + \Re\left(K_{z+}\right)\frac{\tilde{s}_{1z_1}\tilde{s}_{2x_2}}{\tilde{s}_1\tilde{s}_2} - \Im\left(K_{z+}\right)\frac{\tilde{s}_{1z_1}\tilde{s}_{2y_2}}{\tilde{s}_1\tilde{s}_2} \\ & + \Re\left(\mathcal{K}_{+z}\right)\frac{\tilde{s}_{1x_1}\tilde{s}_{2z_2}}{\tilde{s}_1\tilde{s}_2} - \Im\left(\mathcal{K}_{+z}\right)\frac{\tilde{s}_{1y_1}\tilde{s}_{2z_2}}{\tilde{s}_1\tilde{s}_2} \\ & + \frac{\Re\left(K_{++}\right)}{2}\frac{\tilde{s}_{1x_1}\tilde{s}_{2x_2} - \tilde{s}_{1y_1}\tilde{s}_{2y_2}}{\tilde{s}_1\tilde{s}_2} \\ & - \frac{\Im\left(K_{++}\right)}{2}\frac{\tilde{s}_{1x_1}\tilde{s}_{2y_2} + \tilde{s}_{1y_1}\tilde{s}_{2x_2}}{\tilde{s}_1\tilde{s}_2} \\ & + \frac{\Re\left(K_{+-}\right)}{2}\frac{\tilde{s}_{1x_1}\tilde{s}_{2x_2} + \tilde{s}_{1y_1}\tilde{s}_{2y_2}}{\tilde{s}_1\tilde{s}_2} \\ & - \frac{\Im\left(K_{+-}\right)}{2}\frac{\tilde{s}_{1x_1}\tilde{s}_{2y_2} - \tilde{s}_{1y_1}\tilde{s}_{2x_2}}{\tilde{s}_1\tilde{s}_2}.\end{aligned} \tag{B.11}$$

(ii) N_1 is even and N_2 is odd (m_1 is integer, m_2 is half-integer).

(a) $m_1 > q_{\max}/2$ and $m_2 > q'_{\max}/2$ (Ising, I)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = J_{II}\tilde{I}_1\tilde{I}_2 + K_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2}. \tag{B.12}$$

(b) $m_1 > q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$ (Ising, II)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = J_{II}\tilde{I}_1\tilde{I}_2 + K_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + K_{z+}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2+} + K_{z-}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2-} \tag{B.13}$$

$$= J_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}'_{zz'}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z'}}{\tilde{s}_2}, \tag{B.14}$$

where

$$\mathcal{K}'_{zz'} = \sqrt{K_{zz}^2 + \left|K_{z+}\right|^2}, \tag{B.15}$$

$$\tilde{s}_{2z'} = \frac{\Re\left(K_{z+}\right)}{\mathcal{K}'_{zz'}}\tilde{s}_{2x_2} - \frac{\Im\left(K_{z+}\right)}{\mathcal{K}'_{zz'}}\tilde{s}_{2y_2} + \frac{K_{zz}}{\mathcal{K}'_{zz'}}\tilde{s}_{2z_2}. \tag{B.16}$$

(c) $m_1 \leqslant q_{\max}/2$ and $m_2 > q'_{\max}/2$ (non-Ising)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = J_{II}\tilde{I}_1\tilde{I}_2 + K_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + J_{+I}\tilde{s}_{1+}\tilde{I}_2 + J_{-I}\tilde{s}_{1-}\tilde{I}_2. \tag{B.17}$$

(d) $m_1 \leqslant q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$ (non-Ising)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = J_{II}\tilde{I}_1\tilde{I}_2 + K_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + J_{+I}\tilde{s}_{1+}\tilde{I}_2 + J_{-I}\tilde{s}_{1-}\tilde{I}_2 K_{z+}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2+} + K_{z-}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\tilde{s}_{2-}. \tag{B.18}$$

(iii) Both N_1 and N_2 are even (m_1 and m_2 are integer).

(a) $m_1 > q_{\max}/2$ and $m_2 > q'_{\max}/2$ (Ising, I)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = J_{II}\tilde{I}_1\tilde{I}_2 + K_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2}. \tag{B.19}$$

(b) $m_1 > q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$ (non-Ising)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = J_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + \mathcal{J}_{I+}\tilde{I}_1\tilde{s}_{2+} + \mathcal{J}_{I-}\tilde{I}_1\tilde{s}_{2-}. \tag{B.20}$$

(c) $m_1 \leqslant q_{\max}/2$ and $m_2 > q'_{\max}/2$ (non-Ising)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} + \mathcal{J}_{+I}\tilde{s}_{1+}\tilde{I}_2 + \mathcal{J}_{-I}\tilde{s}_{1-}\tilde{I}_2. \tag{B.21}$$

(d) $m_1 \leqslant q_{\max}/2$ and $m_2 \leqslant q'_{\max}/2$ (non-Ising)

$$\begin{aligned}\hat{\mathrm{H}}_{\mathrm{eff}} = {} & \mathcal{J}_{II}\tilde{I}_1\tilde{I}_2 + \mathcal{K}_{zz}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\tilde{s}_{2z_2}}{\tilde{s}_2} \\ & + \mathcal{J}_{I+}\tilde{I}_1\tilde{s}_{2+} + \mathcal{J}_{I-}\tilde{I}_1\tilde{s}_{2-} + \mathcal{J}_{+I}\tilde{s}_{1+}\tilde{I}_2 + \mathcal{J}_{-I}\tilde{s}_{1-}\tilde{I}_2 \\ & + \mathcal{J}_{++}\tilde{s}_{1+}\tilde{s}_{2+} + \mathcal{J}_{+-}\tilde{s}_{1+}\tilde{s}_{2-} \\ & + \mathcal{J}_{-+}\tilde{s}_{1-}\tilde{s}_{2+} + \mathcal{J}_{--}\tilde{s}_{1-}\tilde{s}_{2-}.\end{aligned} \tag{B.22}$$

B.2. Doublet and isotropic spin

The effective Hamiltonian between the anisotropic doublet and isotropic spin (32) reduces as follows:

(i) $m_1 > q_{\max}/2$ (Ising, II)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \sum_{q'=-1}^{1}\mathcal{K}_{zq'}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\mathrm{S}_{2q'}}{S_2} \tag{B.23}$$

$$= \mathcal{K}'_{zz'}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1}\frac{\mathrm{S}_{2z'}}{S_2}, \tag{B.24}$$

where

$$\mathcal{K}'_{zz'} = \sqrt{\sum_{q'=-1}^{1}\left|\mathcal{K}_{zq'}\right|^2}, \tag{B.25}$$

$$\mathrm{S}_{2z'} = \sum_{q'=-1}^{1}\frac{\mathcal{K}_{zq'}\mathrm{S}_{2q'}}{\mathcal{K}'_{zz'}}. \tag{B.26}$$

(ii) $m_1 \leqslant q_{\max}/2$ (non-Ising)

$$\hat{\mathrm{H}}_{\mathrm{eff}} = \sum_{q'=-1}^{1}\left[\mathcal{K}_{zq'}\frac{\tilde{s}_{1z_1}}{\tilde{s}_1} + \mathcal{K}_{+q'}\tilde{s}_{1+} + \mathcal{K}_{-q'}\tilde{s}_{1-}\right]\frac{\mathrm{S}_{2q'}}{S_2}. \tag{B.27}$$

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